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A technique for rapidly determining the conductivity of a conducting polymer film as it is doped in an aqueous or non-aqueous medium is presented. The technique is particularly useful for rapid screening of new potential dopants. It is applicable to redox or protonic acid doping. Experimental conditions can be modified to optimize conductivity and study other related effects; these optimum conditions can subsequently be used for large scale doping by conventional synthetic methods. Results for the oxidative doping of trans-$(CH)_x$ in HBF_4 (48% aq.)/H_2O_2, and in CF_3COOH (80%, aq.)/H_2O_2, for cis-$(CH)_x$ in iodine/CCl_4, and for polyaniline doped in aq. HCl at different pH values are presented.

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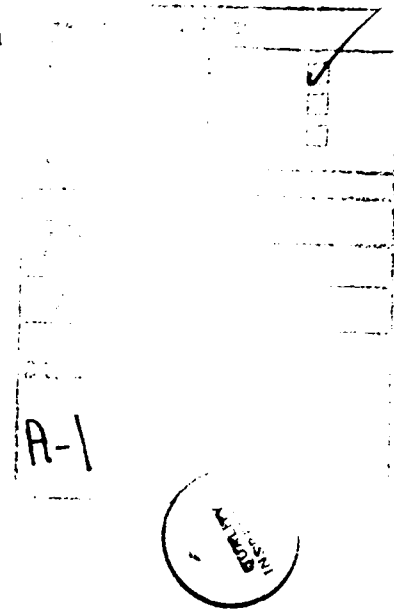
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ABSTRACT

A technique for rapidly determining the conductivity of a conducting polymer film as it is doped in an aqueous or non-aqueous medium is presented. The technique is particularly useful for rapid screening of new potential dopants. It is applicable to redox or protonic acid doping. Experimental conditions can be modified to optimize conductivity and study other related effects; these optimum conditions can subsequently be used for large scale doping by conventional synthetic methods. Results for the oxidative doping of $trans$-$(CH)_x$ in HBF_4 (48% aq.)/H_2O_2, and in CF_3COOH (80%, aq.)/H_2O_2, for cis-$(CH)_x$ in iodine/CCl_4, and for polyaniline doped in aq. HCl at different pH values are presented.

INTRODUCTION

We present a technique for monitoring the in-$situ$ conductivity of a conducting polymer during doping for the simple and rapid: (1) determination of whether or not a given reagent will dope a conducting polymer; (2) determination of the relative effectiveness of different dopants in terms of the conductivity obtained under a given set of experimental conditions; (3) determination of the optimum time, temperature, dopant concentration, etc., conditions for obtaining maximum conductivity; and (4) determination of the conductivity vs doping time relationship.

The in-$situ$ impedance of a conducting polymer film was monitored by a two probe device when surrounded by an aqueous or non-aqueous solution of dopant. In order to minimize electrolysis and related polarization effects in aqueous solution, a 1 kHz AC signal was applied across a polymer film attached to two platinum wire electrodes. The RMS voltage and the current between them was

measured as a function of time. Because the conductivity of these doped films is relatively frequency independent from 10^2 to 10^4 Hz.[1,2], we assume as a first approximation that the impedance is purely resistive and is parallel to the impedance of the solution. The total impedance, Z_{total}, is given by the relationship:

$$\frac{1}{Z_{total}} = \frac{1}{Z_{film}} + \frac{1}{Z_{soln.}}$$

where Z_{total}, Z_{film} and $Z_{soln.}$ are the total impedance, impedance of the polymer film, and impedance of the solution, respectively. If Z_{total} and $Z_{soln.}$ can be determined experimentally, then Z_{film} can be calculated and is taken to approximate the impedance of the film. Since the dimensions of the film between the two platinum electrodes is known, the conductivity, σ(AC, 2-probe, wet), can be determined.

RESULTS

A device was fabricated from Teflon as illustrated in Figure 1(a). Part A had 0.010 inch diameter platinum wires threaded through it. These were sealed in place with paraffin wax. The film to be studied was placed on part A, between the exposed portions of the platinum wires, and part B was clamped on top with the two Teflon clamps. The film was essentially completely exposed on both sides to the doping environment.
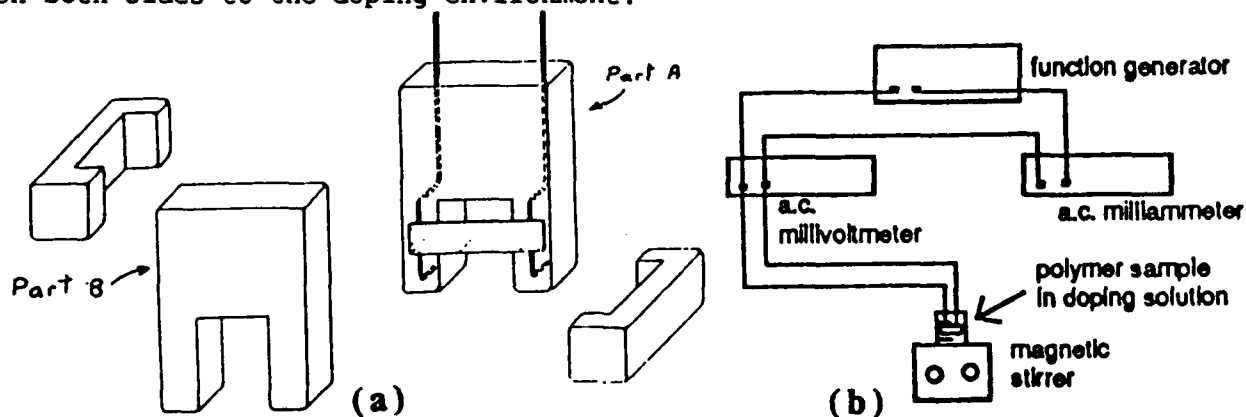

Fig. 1. (a) Diagram of *in-situ* conductivity device; (b) Schematic diagram of circuit used in A.C. conductivity measurements

The experimental setup is illustrated in Figure 1(b). An Iwatsu SG-4101 function generator connected in series with a Keithley 169 digital multimeter in AC current mode was used to generate a 1 kHz sine wave. The Teflon device was connected in series with the function generator and multimeter, and another Keithley 169 multimeter, in AC voltage mode, was connected across the device. A voltage between 60 and 200 mV was typically used.

The Teflon device was immersed in a beaker filled with the dopant solution. Current and voltage measurements were recorded at one minute intervals.

Modification of the doping medium, e.g., addition of oxidant, was made at appropriate times. Z_{total} was calculated ($Z_{total} = v/i$), and plotted vs time. A blank with no film present in the device was run under identical conditions to measure $Z_{soln.}$, the impedance of the solution.

After *in-situ* conductivity measurements were completed the polymer films were removed from the device and dried by pumping on a high vacuum line. Their conductivities, σ(D.C., 4-probe, dry), were then measured. Pieces of free-standing polymer film can be placed in the doping medium and removed at any appropriate time during a given experiment in order to measure their σ(D.C., 4-probe, dry), IR or VIS-UV spectra or to determine their elemental composition, etc.
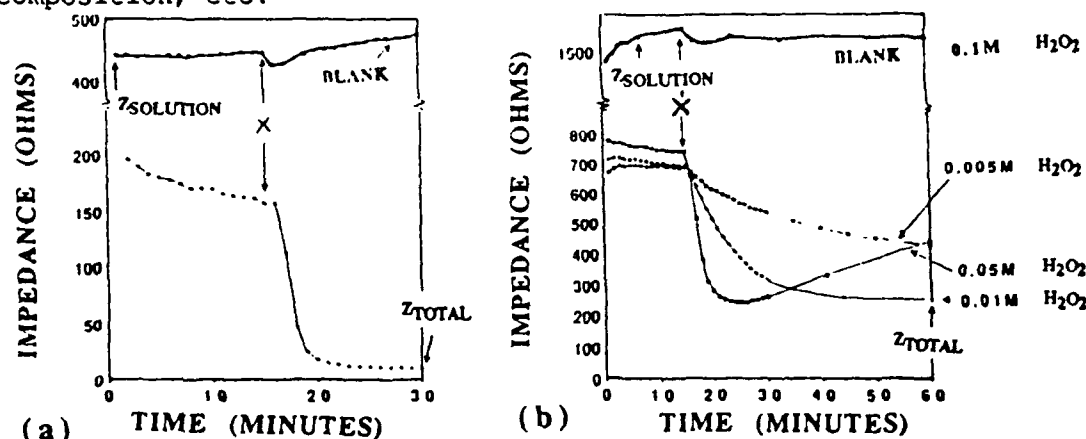

Fig. 2. (a)Doping profile of *trans*-$(CH)_x$ in 48% (aq.)fluoboric acid, HBF_4 (solution made 0.1M in H_2O_2 at "x"); (b)three doping profiles of *trans*-$(CH)_x$ in 80% (aq.) trifluoroacetic acid, CF_3COOH (solution made 0.05-0.005M in H_2O_2 at "x")

The oxidative doping of polyacetylene, where the oxidant, H_2O_2, is different from the dopant anion, $(BF_4)^-$ [3] is illustrated in Figure 2a. A sample of *trans*-$(CH)_x$ in the Teflon device was immersed in 48% aq. HBF_4 and total impedance was plotted as a function of time. The slow decrease in impedance with time up to point "x", where H_2O_2 was added is probably due to the known oxidative doping of $(CH)_x$ by traces of O_2 dissolved in the HBF_4 [3]. At time "x", a quantity of H_2O_2 was added to make the solution 0.1M in H_2O_2. A rapid drop in Z_{total} is evidence for oxidative doping. $Z_{soln.}$ is taken as the value for a blank run under identical conditions; Z_{total} at 30 minutes was used to calculate Z_{film}. A value of σ(AC, 2-probe, wet)= 15.6 S/cm was obtained. After drying the film under dynamic vacuum for 24 hours a value of σ(DC, 4-probe, dry)= 15.7 S/cm was obtained[3].

Figure 2(b) illustrates doping of *trans*-$(CH)_x$ in 80% aqueous trifluoroacetic acid. At time "x" various amounts of H_2O_2 were added in different experiments to give varying concentrations of oxidant. It can be seen that the optimum conductivity is obtained at a concentration of 0.01M H_2O_2. The maximum σ(A.C, 2-probe, wet) at this concentration was 1.6 S/cm.

The doping profile of cis-(CH)$_x$ surrounded by a saturated solution of iodine in CCl$_4$ is shown in Figure 3(a). Since the impedance of the solution is > 20 x 10^6 ohms, Z$_{film}$ is approximately equal to Z$_{total}$. The σ(AC, 2-probe, wet) was 580 S/cm and after drying under dynamic vacuum for 1 hour the corresponding σ(DC, 4-probe, dry) was 606 S/cm.
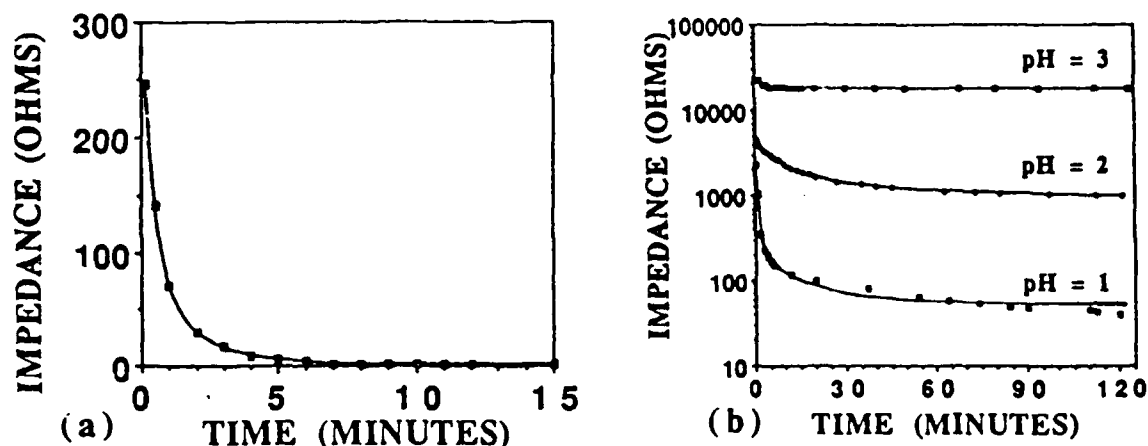

Fig. 3(a) Doping profile of cis-(CH)$_x$ immersed in a saturated solution of iodine in CCl$_4$ (b) Protonic acid (HCl) doping of polyaniline film (emeraldine base) at pH = 1.0, 2.0, and 3.0

Figure 3(b) shows the use of this technique for studying the protonic acid doping of a free-standing film of polyaniline (emeraldine base). The film in the device was immersed in distilled water brought to a specific pH by the addition of HCl. The doping profile is clearly shown. After each of the 120 minute experiments, the polyaniline samples were removed and dried at room temperature under dynamic vacuum for 3 hours and 4-probe dc conductivity values measured. The corresponding conductivities are: (1) pH = 1.0, σ(AC, 2-probe, wet)= 20.2 S/cm, σ(DC, 4-probe, dry)= 5.1 S/cm; (2) pH = 2.0, σ(AC, 2-probe, wet)= 0.66 S/cm, σ(DC, 4-probe, dry)= 0.18 S/cm; (3) pH = 3.0, σ(AC, 2-probe, wet)= 9.2 x 10^{-3} S/cm, σ(DC, 4-probe, dry)= 2.4 x 10^{-3} S/cm.

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